

1 TO WHOM IT MAY CONCERN:

2

3 BE IT KNOWN THAT WE, DAVID W. WARREN, a
4 citizen of the United States of America, residing in
5 Van Nuys, in the County of Los Angeles, and MICHAEL B.
6 DONAHUE, a citizen of the United States of America,
7 residing in La Verne, in the County of Los Angeles,
8 both in the State of California, have invented a new
9 and useful improvement in

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12 **THERMALLY-INTEGRATED LOW TEMPERATURE WATER-GAS SHIFT**

13 **REACTOR APPARATUS AND PROCESS**

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1 BACKGROUND OF THE INVENTION

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3 This invention relates to a process and an
4 apparatus for producing hydrogen for application to
5 fuel cell electric generators.

6 Catalytic reaction apparatus and processes
7 for converting hydrocarbon feedstocks to useful
8 industrial gases, such as hydrogen, is well known in
9 the art. Proton exchange membrane (PEM) fuel cells
10 have emerged as a viable option for the production of
11 disbursed electrical power, typically in the range of
12 2-50 k W, for use in residential and small commercial
13 applications. PEM fuel cells generate electricity by
14 the electrochemical reaction between hydrogen and
15 oxygen.

16 While oxygen is readily available from
17 ambient air, hydrogen must be produced from
18 commercially available fuels, such a natural gas or
19 propane, using methods such as steam reforming. Steam
20 reforming is a process that involves a high temperature
21 catalytic reaction between a hydrocarbon and steam to
22 form a hydrogen-rich product gas, commonly referred to
23 as reformat, that contains significant quantities of
24 carbon monoxide.

1 Since PEM fuel cells have a low tolerance to
2 carbon monoxide, the concentration of carbon monoxide
3 in the reformat must be reduced using a catalytic
4 reaction step known as the water-gas shift reaction.
5 Following the water-gas shift reaction, the
6 concentration of carbon monoxide in the reformat is
7 further reduced to concentrations typically less than
8 10 ppm using a selective oxidation reaction, also
9 referred to as preferential oxidation or PROX. The
10 combination of processes that convert commercial fuels
11 to a reformat suitable for use in a fuel cell is
12 commonly referred to as a fuel processor.

13 As an illustration, Table 1 summarizes the
14 reaction steps of a fuel processor designed to produce
15 a hydrogen-rich gas stream suitable for use in a PEM
16 fuel cell.

17
18 Table 1. PEM fuel processor reaction steps

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20	1. $\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + \text{H}_2$	Steam reforming
21	2. $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$	Water-gas shift
22	3. $\text{CO} + \frac{1}{2}\text{O}_2 = \text{CO}_2$	Selective oxidation

23

24 In typical industrial practice, the water-gas
25 shift reaction is conducted in two separate adiabatic
26 reactors operating at two different temperature

1 regimes. The first reactor, known as the high
2 temperature shift reactor, operates at inlet
3 temperatures typically ranging from about 550°F to
4 650°F. The second reactor, known as the low
5 temperature shift reactor, operates at an inlet
6 temperature typically ranging from about 380°F to
7 450°F. The combination of the two sequential water-gas
8 shift reactions typically reduces the concentration of
9 carbon monoxide in the reformat to less than 1.0
10 volume percent.

11 The use of a low temperature shift reactor is
12 beneficial because the water-gas shift reaction is
13 thermodynamically favored at lower temperatures.
14 However, a high temperature shift reactor is generally
15 required to limit the amount of heat that is released
16 in the low temperature shift reactor.

17 Conventional low temperature shift catalysts
18 comprise a mixture of copper and zinc that are
19 supported on a ceramic carrier. These catalysts
20 promote the water-gas shift reaction at lower
21 temperature, but lose activity if they are exposed to
22 excessively high temperatures due to sintering of the
23 active metals. Therefore, it is generally desirable to
24 limit the maximum temperature of the low temperature
25 shift catalyst to about 500°F in order to achieve long
26 catalyst life.

1 The water-gas shift reaction releases
 2 approximately 9837 calories per gram-mole of carbon
 3 monoxide that is consumed. If the water-gas shift
 4 reaction were conducted using a single adiabatic low
 5 temperature shift reactor, the heat release would
 6 result in a temperature increase across the catalyst
 7 bed that would exceed the desirable temperature limit
 8 for conventional low temperature shift reactors.
 9 Furthermore, the high exit temperature from the water-
 10 gas shift reactor would be thermodynamically less
 11 favorable for achieving high conversions of carbon
 12 monoxide.

13 There is need to minimize the number of
 14 reactors and heat exchangers that are needed to achieve
 15 the objective of high conversion of carbon monoxide for
 16 PEM fuel cell applications, in order to reduce the
 17 size, cost and complexity of the fuel processor.
 18 Therefore, it is desirable to conduct the water-gas
 19 shift reaction using a single reactor vessel that is
 20 maintained within acceptable operating temperature
 21 limits by controlling heat removal from the reactor.

22 The steam reforming reaction requires large
 23 quantities of steam for the conversion of hydrocarbon
 24 to reformat. It is desirable to recover the heat
 25 released from the water-gas shift reaction for the
 26 purpose of generating steam in order to improve the

1 thermal efficiency of the fuel processor. The present
2 invention achieves the objective of temperature control
3 and heat recovery by integrating a lower temperature
4 shift reactor within a steam generator that contains
5 water boiling at a temperature range of about 360°F to
6 400°F, corresponding to a boiler pressure of about 153
7 psia to 247 psia.

8 Because the vessel walls of the lower
9 temperature shift reactor are in heat transfer
10 communication with boiling water, the heat released
11 from the water-gas shift reaction is effectively
12 removed to control the temperature in the catalyst bed
13 within the desired operating temperature range.
14 Furthermore, the heat released from the water-gas shift
15 reaction is beneficially recovered to generate steam
16 that is used in the process. Finally, the steam
17 generator provides a convenient source of heat for
18 heating the catalyst bed during start-up.

19 U.S. Patent 6,086,840 describes a process for
20 making ammonia that mentions use of an isothermal shift
21 reactor that includes heat exchange tubes extending
22 within a vessel packed with catalyst. The heat
23 exchange tubes contain a boiling fluid to remove heat
24 from the catalyst bed.

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[illegible]

3 It is the general object of this invention to
4 provide a novel catalytic reaction apparatus and
5 process for the reduction of carbon monoxide contained
6 in hydrogen-rich gas streams, employing lower
7 temperature shift reactor that is in thermal
8 communication with a steam generator operating in a
9 temperature range that is optimum for catalytic
10 activity and thermodynamic conversion, and allows the
11 recovery of useful waste heat to generate steam needed
12 for a process to convert hydrocarbons feedstocks to
13 useful gases, such as hydrogen. The subject invention
14 is particularly well suited for the production of
15 hydrogen for fuel cells having low tolerance to carbon
16 monoxide.

17 Basically, the invention provides a
18 thermally-integrated low temperature water-gas shift
19 reactor for converting carbon monoxide in the presence
20 of steam to form carbon dioxide and water comprising,
21 in combination,

22 a) a waste-heat recovery steam generator
23 for the beneficial recovery of exothermic reaction heat
24 to generate steam that is used in a process for the

1 conversion of hydrocarbon feedstock into hydrogen-rich
2 gases,
3 b) an outer annulus extending about said
4 waste-heat steam generator,
5 c) a catalyst bed located within said outer
6 region, and through which reformat gases flow,
7 d) the outer region being in heat transfer
8 communication with the steam generator to maintain the
9 catalyst bed within a predetermined temperature range
10 for operation of a low temperature shift reaction.

11 These and other objects and advantages of the
12 invention, as well as the details of an illustrative
13 embodiment, will be more fully understood from the
14 following specification and drawings, in which:

15
16 **DRAWING DESCRIPTION**

17
18 Fig. 1 is a flow diagram of a process that
19 incorporates a thermally-integrated low temperature
20 water-gas shift reactor;

21 Fig. 2 is a schematic showing of apparatus
22 for testing a thermally-integrated low temperature
23 water-gas shift apparatus;

1 Fig. 3a is a schematic showing of a
2 thermally-integrated low temperature water-gas shift
3 reactor apparatus;

4 Fig. 3b is a section taken on lines 3b-3b of
5 Fig. 3a; and

6 Fig. 4 is a schematic showing of an alternate
7 thermally-integrated low temperature water-gas shift
8 reactor apparatus.

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10 **DETAILED DESCRIPTION**

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12 PROCESS AND APPARATUS

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14 The process and apparatus as shown in Fig. 1
15 controls the temperature of a low temperature shift
16 reactor and makes beneficial use of the heat of
17 reaction to generate steam that is employed to produce
18 hydrogen-rich gases containing low concentrations of
19 carbon monoxide from hydrocarbon feedstocks.

20 A reactant mixture at 1 consists of
21 hydrocarbon feedstock 32 and steam 11. The mixture is
22 preheated in an exchanger 2 and introduced into a
23 tubular catalytic reactor 3 that is contained within a
24 combustion chamber 4. The tubular catalytic reactor
25 typically contains a supported Ni catalyst and is

1 commonly referred to in the industry as a steam
2 reformer. Fuel 5 and air 6 are combusted in the
3 chamber 4 to heat the reactant mixture so as to produce
4 a hydrogen-rich stream 7 containing carbon monoxide
5 concentrations typically ranging from 5% to 15%.

6
7 Combustion products 8 from the combustion
8 chamber pass through a flue gas heat exchange coil 9
9 that is contained within a waste heat steam generator
10 10, wherein the combustion products are cooled and steam
11 11 is generated. The cooled combustion products 13 are
12 further cooled by exchanging heat in a feed water
13 exchanger 14 that produces heated water 15 that is
14 supplied to the waste heat steam generator 10.

15
16 The hydrogen-rich stream 7 from the tubular
17 catalytic reactor 3 is cooled in an exchanger 2 to a
18 temperature typically in the range of 400°F-550°F
19 whereupon the cooled steam 18 is introduced into a
20 fixed-bed catalytic reactor 19 shown as surrounding
21 steam generator 10, to effect a water gas shift
22 reaction that converts a portion of the carbon monoxide
23 to hydrogen and carbon dioxide by reaction with steam.
24 The catalyst bed reactor typically contains a supported
25 Cu/Zn catalyst and is commonly known in the industry as
26 a low temperature shift reactor. The walls 20 of the
low temperature shift reactor are in thermal
communication with boiling water contained in the waste

1 heat steam generator. The heat released in the low
2 temperature shift reactor is thus beneficially
3 recovered to generate steam. The carbon monoxide
4 concentration of the process gas 21 exiting the low
5 temperature shift reactor is typically less than 0.5%.

6 The products from the low temperature shift
7 reactor are cooled in a process exchange coil 22 to
8 condense moisture. The condensed moisture 40a is
9 separated in a separator vessel 28 and is pumped at 40b
10 to heat exchanger 14 using pump 41. Make-up water may
11 be added as at 40c. The cooled process gas 29 is mixed
12 with a small quantity of air 30 and is sent to the
13 selective oxidizer reactor 31. The required quantity
14 of ambient air that must be introduced into the process
15 gas depends on the specific performance of the catalyst
16 but typically ranges from 2 to 4 times the quantity
17 necessary to provide a stoichiometric quantity oxygen
18 for the complete oxidation of carbon monoxide.

19 The process gas 32 exiting the selective
20 oxidizer typically contains less than 10 ppm carbon
21 monoxide and is available for use, for instance, in
22 fuel cells having a low tolerance to carbon monoxide.
23 A fuel cell is indicated at 100.

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1 EXPERIMENTAL DATA

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3 Tests were conducted to measure the
4 conversion of carbon monoxide contained in a simulated
5 reformat gas stream that was passed over a commercial
6 Cu/Zn catalyst. The Cu/Zn catalyst was contained
7 within tubular conduit walls that were in thermal
8 communication with a boiling water fluid. The
9 objective of the tests was to quantify the relation
10 between CO conversion and catalyst gas hourly space
11 velocity (GHSV) as a function of the temperature of the
12 boiling water fluid.

13 The experimental test system is shown in Fig.
14 2. The Cu/Zn catalyst 80 was packed in a $\frac{3}{4}$ inch tube
15 81 that was surrounded by a metallic water jacket 82.
16 Steam 83 generated from the water jacket was sent to a
17 condenser 84 and the condensed liquid 85 was returned
18 to the water jacket by natural circulation. An
19 electrical heater 86 was placed on the outer surface of
20 the jacket and a temperature controller 87 was used to
21 control the heat input in order to maintain the water
22 jacket at the desired temperature. A simulated
23 reformat gas mixture 88 was heated in a pre-heater 89
24 to a temperature approximately equal to the boiling
25 water fluid temperature before the gases entered the
26 catalyst bed. The product gases 90 at the exit of the

1 catalyst bed were cooled, condensed and sent to a gas
2 chromatograph for compositional analysis. Table 2
3 summarizes the results for tests conducted using the
4 experimental apparatus.

5

6 Table 2. Carbon Monoxide exit concentration as a
7 function of boiler temperature and catalyst space
8 velocity

9

10 Simulated Reformate Composition at Inlet to Reactor:

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12		Wet Gas	Dry Gas
13	<u>Component</u>	<u>Vol. %</u>	<u>Vol. %</u>
14	CO	5.70	10.0
15	CO ₂	8.55	15.0
16	H ₂	39.90	70.0
17	CH ₄	2.85	5.0
18	H ₂ O	43.00	0.0
19			
20	Total	100.00	100.0

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	Dry Gas GHSV (hr-1)	Boiler Temperature°F	Carbon Monoxide Exit Concentration (Vol.% dry gas)
1			
2			
3			
4	1930	340	3.67
5	762	340	0.62
6	2950	385	2.84
7	2440	385	2.08
8	1930	385	1.70
9	1425	385	0.90
10	1930	398	1.08
11	1425	398	0.55

12
 13 In order to maximize hydrogen yield and
 14 minimize the quantity of carbon monoxide that must be
 15 converted in the selective oxidizer, it is generally
 16 desirable to achieve less than 1.0 vol.% CO in the dry
 17 gas at the exit of the shift reactor. It is desirable
 18 to operate at the maximum space velocity in order to
 19 minimize the size of the catalyst bed.

20 The results show that when the boiler is
 21 maintained at temperatures above about 385°F, the CO
 22 concentration is less than about 1.0 vol.% (dry gas)
 23 for space velocities less than or equal to about
 24 1500hr-1. Higher space velocities can be achieved for
 25 even higher boiler temperatures, however this
 26 necessitates operation at pressures above 250 psig,

1 which may not be desirable for many PEM fuel cell
2 applications.

3 The results indicate that there is an optimum
4 temperature range of operation for the boiler that
5 achieves the objects of minimum catalyst volume,
6 moderate boiler pressure and low CO concentration at
7 the shift reactor exit. This optimum temperature range
8 is approximately 385°F to 400°F.

9
10 THERMALLY-INTEGRATED LOW TEMPERATURE WATER-GAS SHIFT
11 REACTOR APPARATUS

12
13 Apparatus shown in Figs. 3a and 3b controls
14 the temperature of a low temperature shift reactor and
15 makes beneficial use of the heat of reaction to
16 generate steam.

17 In the preferred embodiment, the apparatus
18 comprises an annular catalyst zone 50 within vessel 50a
19 that is concentrically disposed around an inner steam
20 generator zone 51 within vessel 51a. The catalyst zone
21 contains a lower temperature shift catalyst, typically
22 comprising a catalytically active mixture of copper and
23 zinc metals, that promote the water-gas shift reaction
24 at temperatures typically in the range of 370°F to
25 500°F. The catalyst zone is defined by the annular
26 space between an outer wall 52 and an inner wall 53.

1 The steam generator zone is defined in the space inside
2 of the inner wall, a top wall 65, and a tube sheet 66.

3 Reformate containing carbon monoxide enters
4 an inlet conduit 54 that is in communication with the
5 annular catalyst zone. The reformate passes through
6 the catalyst zone, releasing heat due to the exothermic
7 nature of the water-gas shift reaction. The reformate
8 exits from the catalyst zone through an exit conduit
9 55.

10 The inner wall 53 is in thermal contact with
11 the reformate gases flowing through the catalyst zone
12 and boiling water 56 contained in the steam generator
13 zone, the catalyst zone shown as surrounding the steam
14 generation zone. This results in a transfer of heat
15 from the catalyst zone to the steam generator zone in
16 order to maintain the catalyst zone within a defined
17 temperature range that is optimum for conducting the
18 low temperature shift reaction.

19 The steam generator zone contains a heat
20 transfer conduit 57, or a multitude of heat transfer
21 conduits, that is immersed within the boiling water.
22 The heat transfer conduit conveys hot combustion
23 products, such as from the combustion section of a
24 steam reformer, to transfer heat to the boiling water
25 for the purpose of generating steam. The hot
26 combustion products enter an inlet plenum 58 through an

1 inlet conduit 59. The inlet plenum is in communication
2 with the inlet portion 60 of the heat transfer conduit.
3 The hot combustion products exit the heat transfer
4 conduit to an exit plenum 61 that is connected to an
5 exit conduit 62. Steam that is generated from the heat
6 transferred to the steam generator zone through the
7 inner wall 53 and the heat transfer conduit 57 exits
8 the steam generator zone through an exit conduit 68.
9 Water is fed to the steam generator zone through an
10 inlet conduit 69 to maintain the boiling water at a
11 desired level that is sufficient to efficiently remove
12 heat from the inner wall and the heat transfer conduit.

13 The annular catalyst zone 50 may include
14 means to enhance heat transfer between the catalyst bed
15 and the inner wall 53 such as the use of longitudinal
16 fins 70 that are attached to the inner wall and extend
17 a distance into the annular catalyst space. Other heat
18 transfer enhancements such as metal packing within the
19 annular catalyst zone, or active catalyst that are
20 incorporated into highly thermally conductive
21 monoliths, may be beneficially used in the invention.

22

23 EXAMPLE

24 A pipe wall having an outside diameter of 5.5
25 inches defines a waste heat steam generator zone. The
26 pipe wall is in thermal communication with an annular

1 catalyst zone that is concentrically disposed around
2 the waste heat steam generator zone. The space between
3 the 5.5 inch diameter pipe and an outer wall having an
4 8 inch inside diameter define the annular catalyst
5 zone. The annular catalyst zone is packed with 4.8 mm
6 x 2.8 mm low temperature shift catalyst containing
7 principally a mixture of Cu and Zn supported on a
8 ceramic carrier. The packed height of the annular
9 catalyst zone is approximately 12 inches and
10 corresponds to the approximate height of the water
11 contained within the waste heat steam generator zone.
12 The total catalyst volume is approximately 0.184 cubic
13 feet.

14 The waste heat steam generator zone also
15 contains heat transfer conduits that are immersed
16 within the boiling water. The heat transfer conduits
17 consist of 5/8 inch diameter tubes that are formed in a
18 u-tube arrangement having inlet means and exit means
19 that are attached to a single tube sheet. Hot
20 combustion products from a steam reformer are directed
21 to the inlet means of the heat transfer tubes. Cooled
22 combustion products are exhausted from the exit means
23 of the heat transfer tubes.

24 The waste heat steam generator zone is
25 operated at a controlled pressure using a back-pressure
26 regulator that is located on the steam exit conduit.

1 The back-pressure regulator is set at a pressure of 220
2 psia corresponding to a saturated water temperature of
3 390°F.

4 Reformat e from a tubular catalytic reactor is
5 cooled to approximately 510°F and is introduced into
6 the top of the annular catalyst zone. The reformat e
7 exits the bottom of the annular catalyst zone at a
8 temperature of approximately 430°F. The composition
9 and flow rate of the reformat e at the inlet and exit of
10 the annular catalyst zone is shown in Table 3.

11
12 Table 3. Gas composition from thermally-integrated low
13 temperature water-gas shift reactor

14	15	Gas Composition (Volume %)	
		16 <u>Reformat e Inlet</u>	16 <u>Reformat e Exit</u>
17	16 <u>Component</u>		
18	CH ₄	2.1	2.1
19	CO	8.1	0.8
20	CO ₂	7.5	14.7
21	H ₂	52.6	59.8
22	H ₂ O	29.7	22.5
23	Total	100.00	100.0
24			
25	Total Flow, SCFH	280	280
26	Temperature, °F	510	430
27	Pressure, psia	16.7	16.7

1 ALTERNATIVE EMBODIMENT OF THERMALLY-INTEGRATED LOW
2 TEMPERATURE WATER-GAS SHIFT REACTOR APPARATUS
3

4 Fig. 4 depicts an alternative embodiment of
5 the thermally-integrated low temperature water-gas
6 shift reactor apparatus. A helical coil 75 is welded
7 to the surfaces of the inner wall 53 and outer wall 52
8 that define the annular catalyst space. The catalyst
9 is packed within the volumes defined by the helical
10 coil and the inner and outer walls. The gases entering
11 the inlet conduit 54 are directed in a helical manner
12 around the annular space by virtue of the confining
13 helical coil. This increases the velocity of the gases
14 within the catalyst bed for a given space velocity in
15 order to enhance the rate of heat transfer to and from
16 the bed. The helical coil also serves as an extended
17 heat transfer surface to enhance the rate of heat
18 transfer to and from the inner wall of the annular
19 space. Elements the same as those of Fig. 3a bear the
20 same identifying numbers.